

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
28 February 2002 (28.02.2002)

PCT

(10) International Publication Number  
**WO 02/16030 A1**

(51) International Patent Classification?: **B01J 20/32**, 20/28

(21) International Application Number: PCT/EP01/09459

(22) International Filing Date: 15 August 2001 (15.08.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
1015961 18 August 2000 (18.08.2000) NL

(71) Applicant (for all designated States except US): **AKZO NOBEL N.V.** [NL/NL]; Velperweg 76, NL-6824 BM Arnhem (NL).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **VAN STRIEN, Cornelis, Johannes, Govardus** [NL/NL]; Kraaickamp 61, NL-6662 SJ Elst (NL). **SCHOMAKER, Elwin** [NL/NL]; Tuinstraat 2, NL-68882 NX Velp (NL).

(74) Agent: **SCHALKWIJK, Pieter, Cornelis**; Akzo Nobel N.V., Intellectual Property Dept. (Dept. AIP), P.O. Box 9300, NL-6800 SB Arnhem (NL).

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: USE OF AN ADSORBENT FOR THE REMOVAL OF LIQUID, GASEOUS AND/OR DISSOLVED CONSTITUENTS FROM A PROCESS STREAM

(57) Abstract: Use of an adsorbent for the removal of liquid, gaseous and/or dissolved constituents from a process stream, where the adsorbent is a porous material is and/or has been incorporated into a porous material at least 30 vol.% of the pores of which is filled with an extraction liquid and where the affinity between the adsorbent and the constituents to be removed exceeds the affinity between said constituents and the extraction liquid.

WO 02/16030 A1

USE OF AN ADSORBENT FOR THE REMOVAL OF LIQUID, GASEOUS AND/  
OR DISSOLVED CONSTITUENTS FROM A PROCESS STREAM

5

The invention pertains to the use of an adsorbent for the removal of liquid, gaseous and/or dissolved constituents from a process stream.

Such a use is generally known and widely employed in chemical engineering.

One well-known example is the use of a column filled with activated carbon for  
10 the removal of, say, aromatic and/or chlorinated hydrocarbons from a process stream. Once the activated carbon in the column has become saturated, it is generally replaced by fresh activated carbon, while the saturated carbon is reactivated. Meanwhile it has been found that several synthetic adsorbents can be regenerated a number of times with, say, steam.

15 A major drawback to the known process is that it is susceptible to certain inorganic contaminants which are commonly found in very minute concentration, in, say, groundwater to be treated, such as compounds of iron, manganese, calcium, and magnesium which in themselves are not harmful and so do not need to be removed, yet which nevertheless, in the course of time,  
20 may lead to fouling of the adsorbent because a substantial part of its surface area will be covered with said contaminants. To overcome the aforementioned problem it has been proposed in WO 94/03249 that instead of particles having adsorbent properties, particles having extracting properties be used. The extracting particles having a particle size in the range of 0.1 to 10 mm have  
25 pores with a diameter of 0.01 to 50  $\mu\text{m}$  with an extraction liquid immobilised therein.

Although better results can be achieved with these particles, especially after long-term use, than with the well-known adsorbents because of the extracting particles showing no tendency to fouling or a much lower one, the adsorption  
30 capacity of adsorbing materials, especially when the overall concentration of the constituents to be removed does not exceed more than about 100 ppm, as a rule is higher than that of the extracting synthetic particles described above. Consequently, a column containing adsorbents such as activated carbon can be much smaller in size than a column filled with extracting synthetic particles to to

CONFIRMATION COPY

achieve the same result. For that reason there is great need for an adsorbent which combines the advantages of a higher capacity and a lower tendency to fouling, such as is present in extracting synthetic particles.

5 The invention now provides for the use of an adsorbent for the removal of liquid, gaseous and/or dissolved constituents from a process stream which obviates wholly or for the most part the problems which occur when using the known adsorbents.

10 The invention consists in that when employing an adsorbent use is made of a porous material, or a material incorporated into a porous material, at least 30 vol.% of the pores of which is filled with an extraction liquid and where the affinity between the adsorbent and the constituents to be removed exceeds the affinity between said constituents and the extraction liquid.

15 Extraction liquids are used to extract dissolved constituents or to absorb gaseous constituents.

Liquids eligible for use as extraction liquid are known to the skilled person. In the case of liquid/liquid-extraction these generally are liquids with minimal solubility in the medium to be extracted. As a rule, the solubility of these liquids  
20 in the medium to be extracted is not more than 100 g per 1,000 ml.

Very favourable results can be attained using a material at least 50 vol.% of the pores of which is filled with extraction liquid. However, preference is given to a  
25 material at least 90 vol.% of the pores of which is filled with extraction liquid.

The effect of filling the pores with extraction liquid is that when use is made of a porous adsorbent such as activated carbon, its active surface is no longer or virtually no longer subject to deactivation. Surprisingly, it has been found in this  
30 connection that the adsorbent properties of this surface area remain intact wholly or for the most part despite its being covered wholly or for the most part with extraction liquid. Since the extracting capacity of the extraction liquid

remains completely intact, smaller waste treatment plants will suffice for the now proposed use.

5 When use is made of an adsorbent which has been incorporated into a porous material of a different composition, the material having the different composition generally will be a polymeric matrix of the same composition as described in WO 94/03249. In that case preference is given to a porous material where the weight percentage of adsorbent calculated on the overall solids content is at least 2.5 wt.%.  
10

A large number of adsorbents are eligible for use according to the invention. As examples may be mentioned activated carbon, carbon black, synthetic particles based on a wide range of polymers, porous inorganic materials modified with organic substituents or not, such as: porous silica or titania, zeolites such as  
15 molecular sieves, silica gels, porous alumina including the activated types, and clay particles including the exfoliated types. As yet, optimum results have been achieved using an adsorbent selected from the group of activated carbon, zeolites, carbonised sulphonated cross-linked polystyrene, and cross-linked polystyrene.  
20

When the adsorbent is incorporated into a porous material, preference is given to a material obtained by dissolving a polymer in one or more liquid and miscible compounds at a temperature above the upper critical phase separation temperature  $T_c$  in the presence of 2.5 to 80 wt.%, calculated on the overall  
25 solids content, of a material with adsorbent properties which is solid at said temperature, followed by a lowering of the temperature and the forming of a fibre, film, granulate or powder from the polymer filled with the liquid compounds, optionally followed by the removal of at least part of the liquid therefrom and by refilling or filling up with an extraction liquid to at least 30% of  
30 the pore volume.

In that case preference is given to a porous material where the weight percentage of adsorbent is 10 to 70 wt.% and preferably 20 to 60 wt.% of the overall solids content.

As a rule, optimum results are attained with a weight ratio of adsorbent to  
5 extraction liquid in the range of 1/10 to 2/1.

The extraction liquid which is suitable for use according to the invention is a liquid which has the highest possible affinity for the organic constituents to be extracted. Of course, this liquid should be virtually insoluble in the aqueous  
10 solution to be treated and should be immobilised in the porous material in such a way that it is unable to flow from the pores. According to the invention, favourable results have been attained using a liquid in the form of a glycerol ester of one or more, preferably unsaturated fatty acids.

As a rule, favourable results are attained when the immobilised liquid is an oil,  
15 such as palm oil, olive oil, peanut oil, paraffin oil, fish oil such as herring oil, linseed oil, and especially soybean oil and/or castor oil. Optimum results have been attained using paraffin oil and a dialkyl phthalate with an alkyl group having 8 to 16 carbon atoms.

Examples of polymers into which the adsorbent can be incorporated are: low-  
20 pressure polyethene, high-pressure polyethene, polypropylene, polystyrene, acrylonitrile-butadiene-styrene terpolymers, styrene-acrylonitrile copolymers, styrene-butadiene copolymers, poly(4-methyl-pentene-1), and polybutene.

Optimum results have been attained using polyolefin-based polymers. In that case preference is given to the use of a porous material based on  
25 polypropylene.

The thus combined porous material can be used in the form of a fibre, film, granulate or powder, with preference being given to use in the form of a granulate or powder having an average particle diameter of 0.1 to 10 mm. In  
30 this form the material is generally introduced into a column as a packing material. As soon as the concentration of the constituent to be extracted has reached a certain value in the process stream exiting the column, the process

stream supply is halted and the process stream is passed to a column connected in parallel. In the meantime, the material saturated with the constituent to be extracted can be regenerated.

- 5 The principal parameters determining the effectiveness of a column filled with particles with a liquid extraction medium immobilised therein are the equilibrium constant of the distribution of the substance to be extracted over the continuous phase to be extracted and the immobilised phase and the mass transfer rate.
- 10 On the basis of the examples below it will be shown that there is no or virtually no loss of capacity of the oil-filled adsorbents in relation to adsorbents without any oil incorporated therein, while the risk of potential fouling has all but disappeared. By comparing the effectiveness of two columns one of which is filled with extracting synthetic particles without adsorbent while the other is filled
- 15 with extracting synthetic particles with adsorbent, it is further shown that in a column containing the latter particles it took much longer until there was breakthrough.

#### 20 **Preparation of oil-filled adsorbents suitable for use according to the invention**

In a rotary vacuum evaporator the pores of a number of adsorbents were filled with oil, with as much oil being added each time as was commensurate with the pore volume of the adsorbent in question. The filling took place at a temperature of 70°C and under a pressure of less than 50 mbar. The filling time was highly

25 dependent on the type of adsorbent and the selected pressure and ranged from 30 minutes to 12 hours.

Diisodecyl phthalate was selected as the oil, and the selected adsorbents were: Ambersorb® 563, black spherical beads with a specific surface area of 550 m<sup>2</sup>/g (ex Rohm and Haas Co.),

30 activated carbon SA Super® (ex Norit), and XAD-4® (ex Rohm and Haas), a copolymer of styrene and divinyl benzene

The composition of the oil-filled adsorbents is listed in Table 1.

Table 1

type with oil-filled adsorbent	adsorbent	wt.% of adsorbent	wt.% of diisodecyl phthalate
P1	Ambersorb <sup>®</sup> 563	66.2	33.8
P2	activated carbon SA Super <sup>®</sup>	42.5	57.5
P3	XAD-4 <sup>®</sup>	50	50

- 5 The preparation of an oil-filled synthetic granulate based on polypropylene, hereinafter referred to as P4, was carried out in a manner corresponding to that described in WO 94/03249. In this process there were mixed in a twin-screw extruder at 210°C 30 parts by weight (pbw) of polypropylene (type Eltex HCW280<sup>®</sup>) and 70 pbw of a mixture composed of 80 parts of diisodecyl
- 10 phthalate and 20 parts of castor oil. The solution was extruded through a spinneret plate with orifices of 1.2 mm, whereupon the resulting cable strand was laid on a cooling belt and the chopped up into beads of about 1 mm long. Finally, in a manner analogous to that given for the preparation of P4 a type P5 was prepared, with activated carbon of the Norit SA Super<sup>®</sup> type being used as
- 15 adsorbent. To this end 30 pbw of polypropylene (type Eltex HCW280<sup>®</sup>) and 30 pbw of activated carbon (type SA Super<sup>®</sup>, ex Norit; BET 900 m<sup>2</sup>/g; 3% > 150µm, 40% < 10µm) were mixed with 40 pbw of a mixture composed of 80 parts of diisodecyl phthalate and 20 parts of castor oil.
- Types P6 and P7 were prepared in an analogous manner, with the proviso that
- 20 P6 contained 15 wt.% of activated carbon and P7 contained 15 wt.% of Ambersorb 563<sup>®</sup>. Furthermore, types P8 through P11 were prepared in an analogous manner, containing silicalite EZ072 as an adsorbent.

The composition of types P4 through P7 is listed in Table 2.

Table 2

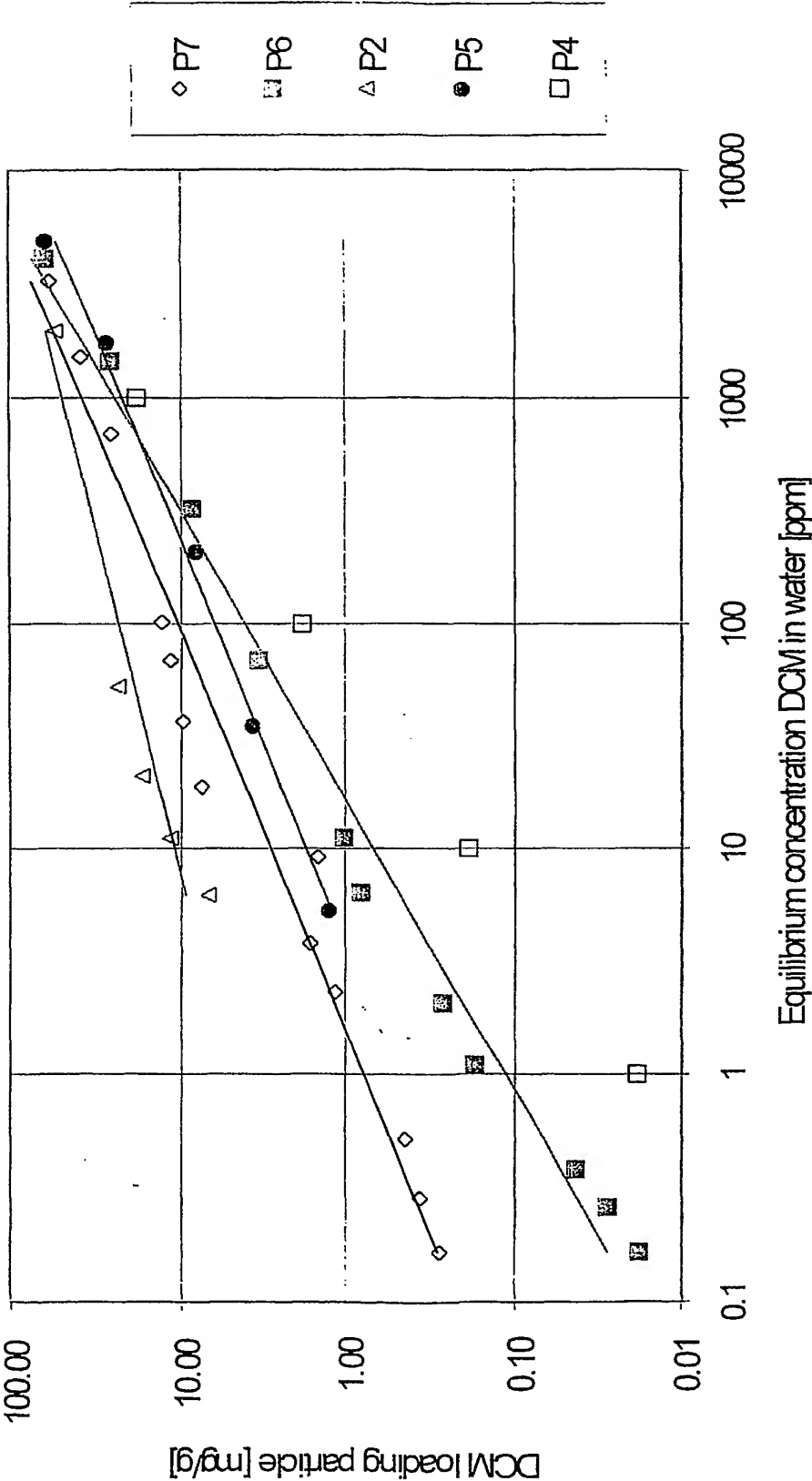
type with oil-filled matrix and, optionally, adsorbent	adsorbent	matrix	wt. % adsorbent/-matrix	wt. % diisodecyl phthalate/castor oil (80/20)
P4	none	polypropylene	0/30	70
P5	activated carbon	polypropylene	30/30	40
P6	activated carbon	polypropylene	15/30	55
P7	Ambersorb 563®	polypropylene	15/30	55
P8	silicalite EZ072	polypropylene	5.0/25.3	69.7
P9	silicalite EZ072	polypropylene	14.9/29.9	55.2
P10	silicalite EZ072	polypropylene	16.2/24.8	59.0
P11	silicalite EZ072	polypropylene	25.0/20.0	55.0

#### 5 Example I

The example below shows how the adsorption capacity of adsorbents filled with extraction liquid (oil) for a particular type of contaminant can be determined. The measurements were performed with methylene chloride (DCM) as contaminant in water at concentrations ranging from 0.1 to about 5,000 ppm and are the result of a number of shaking tests in which a certain quantity of adsorbent was added to a measured quantity of water with a known quantity of methylene chloride dissolved therein. The mixture of solution and adsorbent in each case was stirred for 24 hours, after which the remaining concentration of methylene chloride was again determined. From the difference in concentration the quantity of methylene chloride adsorbed by the adsorbent could be calculated. By varying both the quantity of adsorbent and the starting concentration over a wide concentration range the capacity of the particles as a function of the equilibrium concentration could be determined. The result of the measurements is shown in Figure 1.



Figure 1



Example II

In the example below three columns were compared, one filled with extracting synthetic particles without adsorbent and the two others holding extracting  
5 synthetic particles with adsorbent, and it was shown that water treatment with a column containing the latter particles could be continued much longer before breakthrough occurs and that the column has to be regenerated.

The experiment was carried out using, on the one hand particles filled with extracting agent without an adsorbent being present (P4) and, on the other,  
10 particles into which in addition to an extracting agent an adsorbent was incorporated: either 15 wt.% Ambersorb 563 (P7) or 16 wt.% silicalite EZ072 (P10).

Figure 2 clearly shows that under virtually comparable conditions breakthrough occurred much more quickly when particles without adsorbent (P4) were used  
15 than when use was made of particles containing an adsorbent as well as an extracting agent (either P7 or P10).

The quantity of adsorbent, the rate of flow of water to the column, and the methylene chloride concentration during the three experiments are listed in  
Table 3. The internal diameter of the columns used in these experiments was 5  
20 cm.

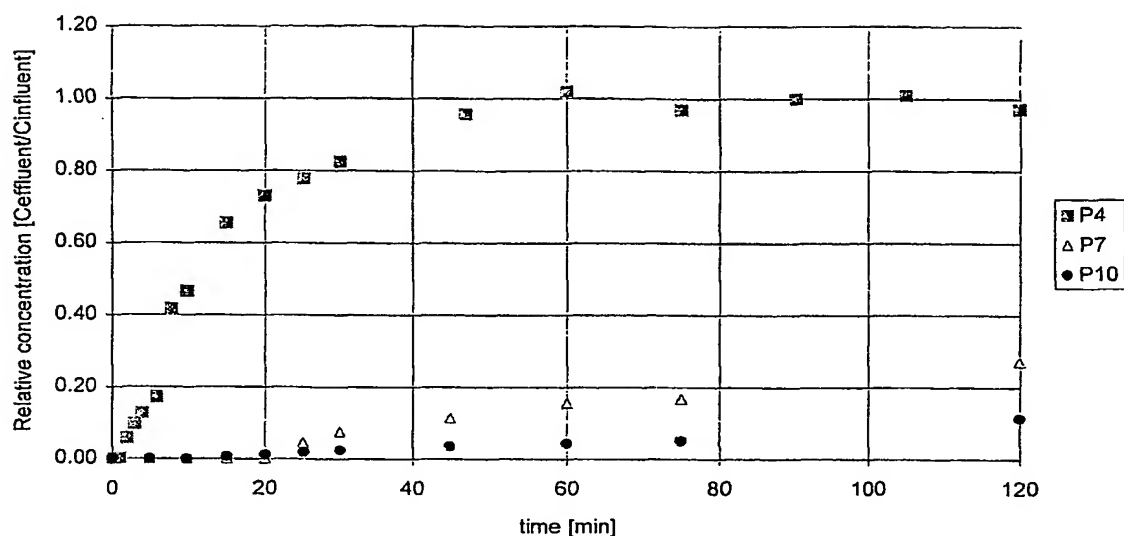
Table 3

type of particle	P4	P7	P10
quantity of particles, g	175	185	202
water rate of flow to column, l/h	7.3	6.5	6.6
influent concentration DCM, ppm	40	55	48

25 The breakthrough curve, where the effluent concentration divided by the influent concentration is plotted against the time is shown in Figure 2 for the three particles (P4, P7 and P10).

Figure 2

Figure 2



### 5 Example III

In the example below it is shown that the adsorption capacity of adsorbents and the extraction capacity of the extracting agent used do not decrease (or hardly decrease) when the adsorbent is wholly or partially embedded in an extraction liquid.

- 10 For the results shown in Figure 1 the adsorption capacity of the adsorbent used in these particles was determined and this capacity was compared with the capacity of the pure adsorbent as determined experimentally.

For the determination of the adsorption capacity it was determined first of all how much methylene chloride is incorporated into the diisodecyl phthalate present in the particle under the given circumstances, based on the measured distribution equilibria. Next, the adsorption capacity of the adsorbent in the particle is determined by dividing the remaining quantity of DCM by the quantity of adsorbent that is present. The thus determined adsorption capacity of the adsorbent in the particle is compared with the capacity of pure adsorbent.

Figure 3 shows the thus determined capacity for activated carbon covered with extracting agent as determined in the particles P2, P5, and P6, as well as the capacity of pure activated carbon for comparative purposes.

- 5 Figure 4 shows the capacity of pure Ambersorb<sup>®</sup> 563 and of Ambersorb<sup>®</sup> 563 as present in particle P7.

It is clear from Figures 3 and 4 that the adsorbent properties of the adsorbent are retained virtually completely when the adsorbent is covered with extraction  
10 liquid.

Figure 3

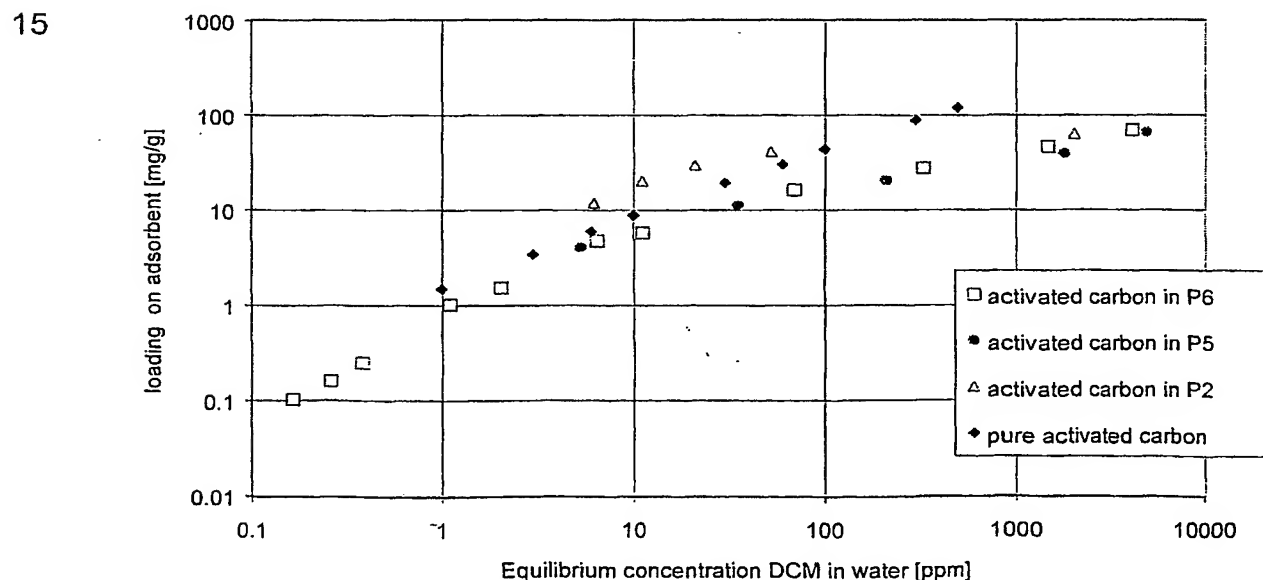
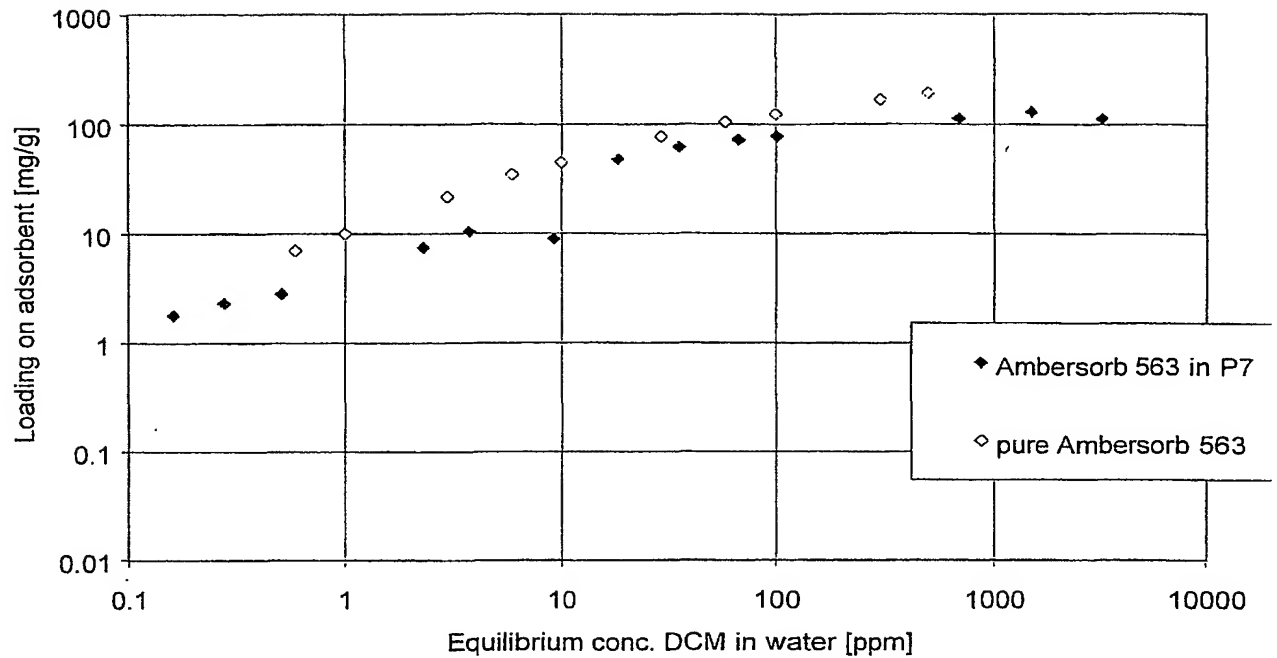


Figure 4



## 5 Comparison example

To illustrate the difference in particle capacity it was determined how much adsorbent is required to achieve a desired reduction of the concentration.

The required quantity of adsorbent covered with oil or not for effecting a change in concentration from 1,000 to 10 ppm DCM in a stirred vessel containing 1 m<sup>3</sup>

10 (1,000 kg) of water is shown in Table 4:

Table 4

type with matrix filled with oil and, optionally, adsorbent	adsorbent	matrix	wt.% adsorbent/matrix	wt.% diisodecyl phthalate, or (80/20) diisodecyl phthalate/castor oil	kg adsorbent required for change in concentration from 1,000 to 10 ppm DCM
P2	activated carbon	none	42.5	57.5	90
P4	none	polypropylene	0/30	70	5,440
P5	activated carbon	polypropylene	30/30	40	570
P6	activated carbon	polypropylene	15/30	55	1,465
P7	Ambersorb 563 <sup>®</sup>	polypropylene	15/30	55	350

Example IV

5

This example again shows that the adsorption capacity of adsorbents and extraction capacity of the extracting agent used do not decrease (or hardly decrease) when the adsorbent is wholly or partly embedded in an extraction liquid. The methylene chloride adsorption capacity of silicalite as present in the particles P8 through P11 was determined and this capacity was compared with the capacity of the pure adsorbents as determined experimentally, in a similar manner as described in Example III. It was determined how much methylene chloride is incorporated into the diisodecyl phthalate present in the particle under the given circumstances, based on the measured distribution equilibria.

10

15

Next the adsorption capacity of the zeolite in the particle was determined by dividing the remaining quantity of DCM by the quantity of adsorbent that is present. The thus determined adsorption capacity of the adsorbent in the particle was compared with the capacity of pure adsorbent.

20

Figure 5 shows the capacity of particles P8 through P11 and of pure silicalite, and Figure 6 shows the capacity of silicalite in P8 through P11 and again for

pure silicalite. It is clear from Figure 6 that the adsorbent properties of the silicalite EZ072 were retained virtually completely when the adsorbent was covered with extraction liquid.

5 Figure 5

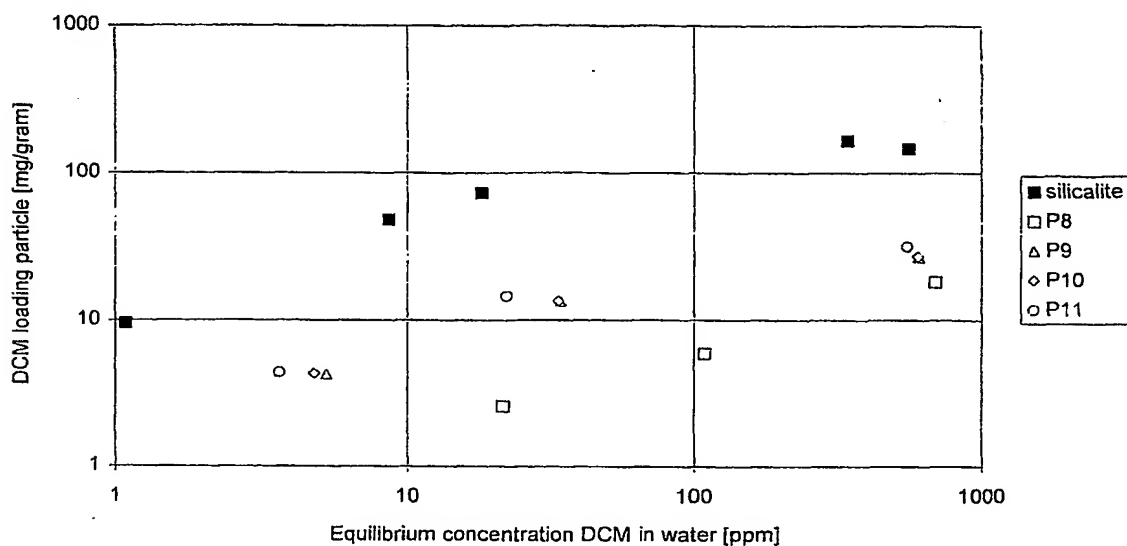
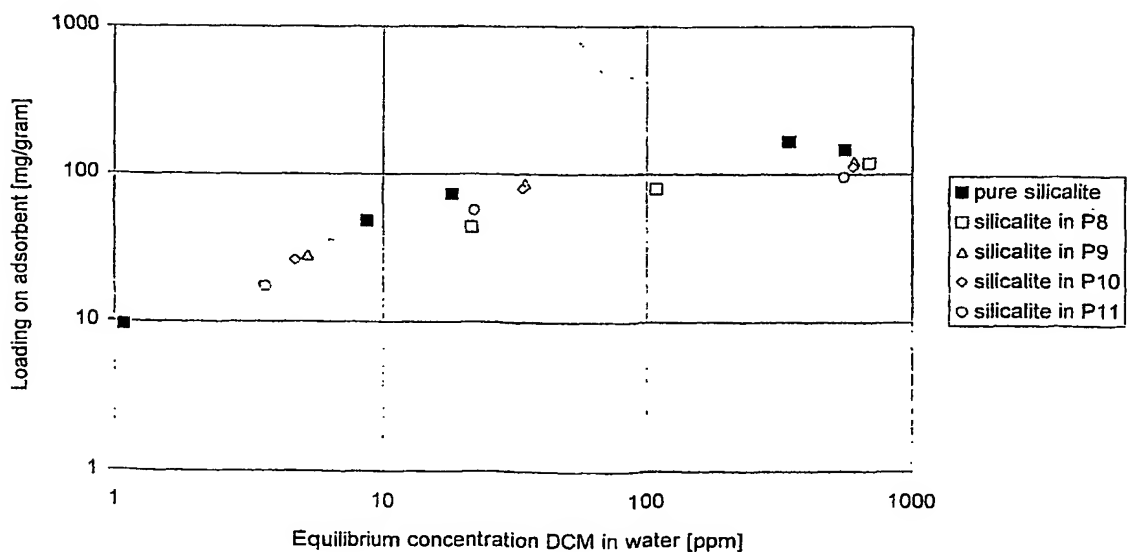


Figure 6



## Claims

1. Use of an adsorbent for the removal of liquid, gaseous and/or dissolved constituents from a process stream, characterised in that the adsorbent is a porous material and/or has been incorporated into a porous material at least 30 vol.% of the pores of which is filled with an extraction liquid and where the affinity between the adsorbent and the constituents to be removed exceeds the affinity between said constituents and the extraction liquid.
2. Use according to claim 1 wherein at least 50 vol.% of the pores is filled with an extraction liquid.
3. Use according to claim 1 wherein at least 90 vol.% of the pores is filled with an extraction liquid.
4. Use according to claim 1 wherein at least 2.5 wt.% of the porous material takes the form of an adsorbent.
5. Use according to claim 1 wherein the adsorbent is selected from the group of activated carbon, zeolites, carbonised sulphonated cross-linked polystyrene, and cross-linked polystyrene.
6. Use according to claim 1 wherein the adsorbent is incorporated into a porous material obtained by dissolving a polymer in one or more liquid and miscible compounds at a temperature above the upper critical phase separation temperature  $T_c$  in the presence of 2.5 to 80 wt.%, calculated on the overall solids content, of a material with adsorbent properties which is solid at said temperature, followed by a lowering of the temperature and the forming of a fibre, film, granulate or powder from the polymer filled with the liquid compounds, optionally followed by the removal of at least part of



the liquid therefrom and by refilling or filling up with an extraction liquid to at least 10% of the pore volume.

- 5        7. Use according to claim 6 wherein the weight percentage of adsorbent amounts to 20 to 60 wt.% of the overall solids content.
8. Use according to claim 6 wherein the weight ratio of adsorbent to extraction liquid is in the range of 1/10 to 2/1.
- 10    9. Use according to claim 1 wherein the extraction liquid is diisodecyl phthalate.
- 15    10. Use according to claim 1 wherein the adsorbent or the porous material into which the adsorbent has been incorporated is present in the form of a granulate or powder having a particle size of 0.1 to 10 mm.
11. Use according to claim 1 wherein the material after becoming saturated with the constituent to be extracted is regenerated with steam.

## INTERNATIONAL SEARCH REPORT

In International Application No

FCI/EP 01/09459

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 B01J20/32 B01J20/28

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B01J B01D C02F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, EPO-Internal, PAJ

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 91 05859 A (THE UNITED STATES OF AMERICA) 2 May 1991 (1991-05-02) page 12, line 7,8; claims 1-3 page 7, line 17 - line 23 page 5, line 13 - line 15 page 1, line 6 - line 9 ---	1-5
A	GB 1 535 481 A (INSTITUT FRANCAIS DU PETROLE) 13 December 1978 (1978-12-13) page 4; example 6 ---	1-5,10
A	EP 0 761 304 A (AKZO NOBEL) 12 March 1997 (1997-03-12) claim 1 ---	1,6
A	US 3 960 762 A (R. KROEBEL) 1 June 1976 (1976-06-01) claims 25,30 ---	1-5
-/--		

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

## \* Special categories of cited documents:

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

\*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

\*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

\*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

\*Z\* document member of the same patent family

Date of the actual completion of the international search

28 November 2001

Date of mailing of the international search report

06/12/2001

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Hilgenga, K

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 01/09459

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 842 745 A (W. WEILER) 27 June 1989 (1989-06-27) column 3, line 3 - line 41 -----	1-5
A	US 5 102 512 A (J.M. LAMERANT) 7 April 1992 (1992-04-07) claims 1,7 -----	1-4
A	US 4 711 863 A (M. STREAT) 8 December 1987 (1987-12-08) column 2, line 12 - line 44 -----	1-4

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 01/09459

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 9105859	A	02-05-1991	AU 627630 B2 AU 6645190 A CA 2044167 A1 EP 0450047 A1 JP 3504467 T WO 9105859 A1 US 5279745 A	27-08-1992 16-05-1991 19-04-1991 09-10-1991 03-10-1991 02-05-1991 18-01-1994
GB 1535481	A	13-12-1978	FR 2340910 A1 BE 851080 A1 DE 2704569 A1 IT 1075554 B JP 52098676 A NL 7701328 A	09-09-1977 04-08-1977 18-08-1977 22-04-1985 18-08-1977 15-08-1977
EP 761304	A	12-03-1997	AT 185090 T DE 69604466 D1 DE 69604466 T2 DK 761304 T3 EP 0761304 A1 ES 2138786 T3 JP 9103605 A US 5750030 A	15-10-1999 04-11-1999 23-03-2000 03-04-2000 12-03-1997 16-01-2000 22-04-1997 12-05-1998
US 3960762	A	01-06-1976	DE 2162951 A1 AR 193157 A1 AT 334868 B AT 1070672 A BE 792928 A1 CA 1014689 A1 CH 597307 A5 CS 171740 B2 DD 102391 A5 ES 409725 A1 FR 2163763 A1 GB 1407257 A IL 41094 A IT 974064 B JP 1106093 C JP 48070594 A JP 56048828 B NL 7217118 A ,B OA 4296 A RO 63158 A1 SE 396016 B SU 520052 A3 ZA 7208893 A	20-06-1973 30-03-1973 10-02-1977 15-06-1976 18-06-1973 26-07-1977 31-03-1978 29-10-1976 12-12-1973 16-11-1975 27-07-1973 24-09-1975 29-02-1976 20-06-1974 30-07-1982 25-09-1973 18-11-1981 20-06-1973 31-12-1979 15-06-1978 05-09-1977 30-06-1976 26-09-1973
US 4842745	A	27-06-1989	DE 3618698 A1 AT 87278 T AT 102585 T DE 3784968 D1 DE 3789323 D1 EP 0248429 A2 EP 0457359 A1	10-12-1987 15-04-1993 15-03-1994 29-04-1993 14-04-1994 09-12-1987 21-11-1991
US 5102512	A	07-04-1992	FR 2616157 A1 AT 62466 T	09-12-1988 15-04-1991

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 01/09459

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5102512	A	AU 604325 B2	13-12-1990
		AU 1696788 A	08-12-1988
		BR 8802654 A	27-12-1988
		CA 1337021 A1	19-09-1995
		CN 88103282 A ,B	21-12-1988
		DE 3862346 D1	16-05-1991
		EP 0297998 A1	04-01-1989
		GR 3001757 T3	23-11-1992
		HU 209448 B	28-06-1994
		IE 61367 B	02-11-1994
		IN 169596 A1	16-11-1991
		JP 1004435 A	09-01-1989
		SU 1813111 A3	30-04-1993
		YU 106588 A1	30-04-1990
US 4711863	A	08-12-1987	
		CA 1263641 A1	05-12-1989
		DE 3672278 D1	02-08-1990
		EP 0252912 A1	20-01-1988
		ES 552932 D0	16-10-1987
		ES 8800075 A1	01-01-1988
		WO 8605521 A1	25-09-1986
		GB 2172293 A ,B	17-09-1986
		IL 78122 A	31-10-1989
		JP 62502179 T	27-08-1987
		NO 864499 A	12-01-1987
		ZA 8601799 A	25-11-1987

This Page Blank (uspto)